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1. Document ID: US 20020019469 A1

L9: Entry 1 of 2 File: PGPB Feb 14, 2002

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DOCUMENT-IDENTIFIER: US 20020019469 A1

TITLE: Polyacetal resins with reduced formaldehyde odor

PUBLICATION-DATE: February 14, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Mori, Hiroshi	Tochigi-ken	DE	JP	
Kassal, Robert James	Wilmington		US	
Shinohara, Kenichi	Tochigi-ken		JP	

US-CL-CURRENT: 524/247

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw. Desc | Image

2. Document ID: WO 9414888 A1

L9: Entry 2 of 2 File: EPAB Jul 7, 1994

PUB-NO: WO009414888A1
DOCUMENT-IDENTIFIER: WO 9414888 A1
TITLE: POLYACETAL RESIN COMPOSITION

PUBN-DATE: July 7, 1994

INVENTOR-INFORMATION:

NAME	COUNTRY
SHINOHARA, KENICHI	JP

US-CL-CURRENT: 524/48
INT-CL (IPC): C08L 3/02; C08L 5/16; C08K 5/15; C08K 5/07
EUR-CL (EPC): C08K005/07; C08L059/00, C08K005/15

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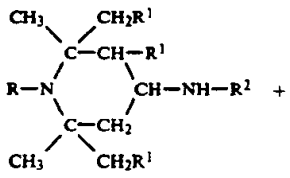
methods well known in the art from the corresponding mono esters of the dicarboxylic acids and chlorinating agents such as thionyl chloride, phosgene, phosphorous trichloride or phosphorous pentachloride.

PREPARATION METHOD B

The N-(2,2,6,6-tetraalkyl-4-piperidinyl)amide-hydrazides of Formula VIII may also be prepared by reacting the amino compounds of Formula II with essentially equivalent amounts or an excess of a dicarboxylic acid diester of Formula VI to form the intermediate half ester-half amide of Formula VII. The intermediate VII is then reacted with hydrazine or hydrazine hydrate to form the compounds I where R^4 is hydrogen and R^6 is the same as R^3, designated as Formula VIII, with the provisos that R^6 may not be an alkenylene or ethylene diradical and R^2 and R^6 are not linked together.

The reaction sequence of Method B is illustrated by the following equations:



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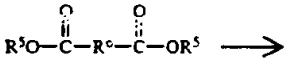

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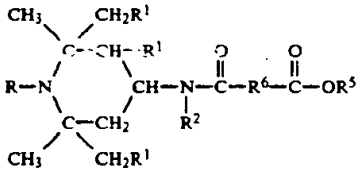
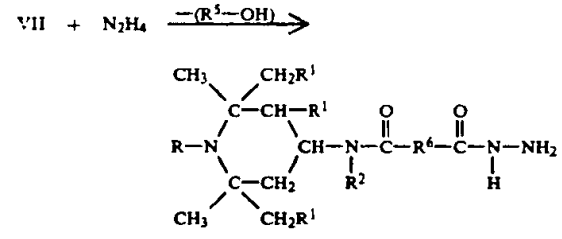


VII



VIII

In the equations for Method B, R, R^1, R^2 and R^5 are as previously defined, R^6 is the same as R^3, except R^6 may not be an alkenylene diradical or an ethylene diradical and R^2 and R^6 are not linked together to form a lactam ring.

The reactions are preferably run neat, or in alcoholic or glycol solvents and most preferably neat or in methanol if the diesters are activated. The amines II react quite readily with the oxalic acid diesters VI at room temperature and gentle cooling is advisable in the early stages of the reaction to minimize side reactions. In the case of the other diesters (i.e., where R^6 is not a direct bond), heating or refluxing is necessary. The reactions can be monitored by gas chromatography and depending upon the starting amines and diesters, the reaction temperature can be adjusted up or down to speed up or slow down the reaction. In some cases it is preferable to distill off the alcohol as it forms.

When using dialkyl oxalates in methanol or ethanol, it is preferable to cool the alcohol solution of the oxalate below room temperature (5°–10° C.) before adding the amine and then allowing the temperature to rise to room temperature or above over the course of ½ to 1 hour. After the oxalate is converted to the half ester-half amide VII, an equivalent amount of hydrazine or hydrazine hydrate is added. The hydrazine readily reacts with the half-ester to form the amide-hydrazide. Any unreacted dialkyl oxalate is readily converted to insoluble oxalic acid dihydrazide which is removed by filtration. Depending upon the amount of alcohol present, the reaction mixture may have to be heated to dissolve all the product before filtering off the oxalic acid dihydrazide. The product is isolated by stripping off the solvent or by cooling the filtrate and crystallizing out the product.

When using dialkyl oxalates, the first step of the reaction sequence is preferably run in excess dialkyl oxalate to minimize side products. The excess oxalate is removed, preferably by vacuum stripping, and the hydrazinolysis of the intermediate half ester-half amide is preferably carried out in methanol, ethanol, propanol, or isopropanol.

When using diesters of other dicarboxylic acids, more severe heating conditions are required for both steps. However, the reactions can be monitored by infrared spectroscopy, or liquid or gas chromatography, and the heating conditions and length of reaction adjusted accordingly.

Suitable amines II are those illustrated for Method A. Likewise the same hydrazines are suitable for both Methods A and B. Suitable diesters include, for example and without limitation, the methyl, ethyl, propyl, isopropyl and phenyl diesters or mixtures thereof of oxalic, malonic, substituted malonic, glutaric, adipic, 2-methylglutaric, 3-methylglutaric, 2,2-dimethylglutaric, 3,3-dimethylglutaric, pimelic, adipic, suberic, azelaic, sebacic, undecanedioic, 1,10-decanedicarboxylic, 1,12-dodecanedicarboxylic, o-, m- and p- phthalic and 3,3'-thiodipropionic acids. Diesters of fumaric acid and succinic acid were found to be unacceptable in this method.

Preferably, the amine is 4-amino-2,2,6,6-tetramethylpiperidine, the diester is diethyl oxalate, and the hydrazine is 85% hydrazine hydrate, the first step is run in excess diethyl oxalate and the hydrazinolysis step is run in methanol.

PREPARATION METHOD C

The N-(2,2,6,6-tetraalkyl-4-piperidinyl)amide-hydrazides of Formula VIII may also be prepared by reacting hydrazine or hydrazine hydrate with an excess of a dicarboxylic acid diester of Formula VI to form the intermediate half ester-half hydrazide of Formula IX (U.S. Pat. No. 3,022,345, Example 5A). The intermediate IX is then separated from the excess diester and reacted with essentially an equivalent amount or slight excess of an amino compound of Formula II. The method is limited to those compounds of Formula I wherein R^6 is the same as R^3, and is not an alkenylene or ethylene diradical, R^4 is hydrogen and R^2 and R^6 are not linked together, designated as Formula VIII.

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L9	l1 near2 l6	2	L9
L8	l1 near l6	0	L8
L7	l1 and l6	18	L7
L6	reduced formaldehyde	224	L6
L5	polyacetal and monoethanolamine [clm]	20	L5
L4	polyacetal and monoethanolamine [ab]	1	L4
L3	polyacetal and monoethanolamine [ti]	0	L3
L2	polyacetal and monoethanolamine	360	L2
L1	polyacetal	20778	L1

water, but advantageously it can also be carried out without a solvent. The temperature is preferably elevated and in the range from about 40° C. to about 200° C. and in particular from about 60° C. to about 140° C. The reaction time is several hours and in particular about 2 to about 24 hours. Preferably, the reaction is carried out in an inert atmosphere, for example, under nitrogen. The alcohol formed is advantageously removed from the reaction mixture and preferably is distilled off.

The intermediate XI is isolated and dissolved in a polar solvent and converted to the hydrazide by stirring with an equivalent amount or slight excess of hydrazine or hydrazine hydrate. The reaction proceeds at room temperature, but may be accelerated by heating. Preferably, the hydrazinolysis reaction is carried out in methanol or ethanol at about 10° C. to about 65° C. The products of Formula XII can be purified by recrystallization from the lower alcohols.

Non-limiting examples of suitable itaconate diesters include the dimethyl, diethyl, dipropyl, diisopropyl and dibutyl diesters.

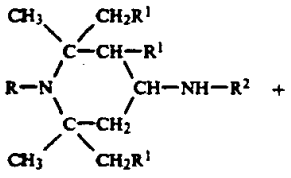
Non-limiting examples of suitable 4-amino-2,2,6,6-tetraalkylpiperidines (Formula IIA) include 4-amino-2,2,6,6-tetramethylpiperidine, 4-amino-1,2,2,6,6-pentamethylpiperidine, 4-amino-2,6-diethyl-2,3,6-trimethylpiperidine, and 4-amino-2,6-diethyl-1,2,3,6-tetramethylpiperidine.

Preferably, the diester is dimethyl itaconate, the amine IIA is 4-amino-2,2,6,6-tetramethylpiperidine and the hydrazine is 85% hydrazine hydrate.

PREPARATION METHOD E

The N-(2,2,6,6-tetraalkyl-4-piperidinyl)amide-hydrazides of Formula I, where R^4 is hydrogen and R^3 is a direct bond, designated as Formula XV, may also be prepared by reacting the amino compounds of Formula II with essentially equivalent amounts of an oxamate of Formula XIII, where R^5 is lower alkyl or phenyl, preferably methyl or ethyl, to form an N-(2,2,6,6-tetraalkyl-piperidinyl)oxamide of Formula XIV. The N-(2,2,6,6-tetraalkyl-4-piperidinyl)oxamide is isolated and then reacted with an equivalent or excess of hydrazine or hydrazine hydrate to displace ammonia and form the compounds of Formula I where R^4 is hydrogen and R^3 is a direct bond.

The reaction sequence of Method E is illustrated by the following equations.



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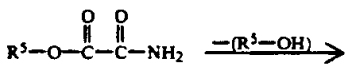

XIII

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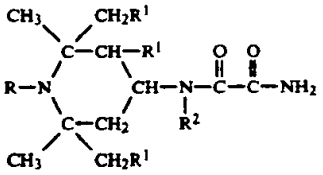
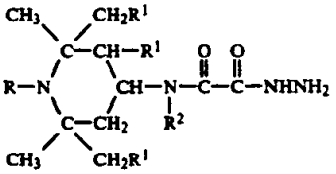


XIV

XIV + N_2H_4 $\xrightarrow{-NH_3}$



XV

In the equations for Method E, R, R^1, R^2 and R^5 are as previously described.

The reactions are preferably run in alcohol or glycol solvents and most preferably methanol or ethanol. The amines II, preferably where R and R^2 are hydrogen, react quite readily with the alkyl oxamates at room temperature. Preferably, the reaction is carried out at about 20° C. to about 40° C. to avoid side reactions. The reaction can be monitored by gas chromatography and depending upon the starting amine, the reaction temperature can be adjusted up or down to speed up or slow down the reaction. The oxamide XIV is separated from the reaction by filtration and the filtrate containing some oxamide XIV can be recharged with additional alkyl oxamate XIII and amine II and the reaction repeated.

The oxamide XIV is slurried with fresh alcohol, an excess of hydrazine or hydrazine hydrate added and the reaction heated to reflux. The conversion of the oxamide XIV to the hydrazide XV can be followed by gas chromatography. The hydrazides XV are generally soluble in hot alcohol and crystallize out of solution upon cooling. Further purification can be achieved by recrystallization from methanol, ethanol or isopropanol.

Non-limiting examples of suitable amines II include: 4-amino-2,2,6,6-tetramethylpiperidine, 4-amino-2,6-diethyl-2,3,6-trimethylpiperidine, 4-amino-1,2,2,6,6-pentamethylpiperidine and 4-amino-2,6-diethyl-1,2,3,6-tetramethylpiperidine.

Non-limiting examples of suitable oxamate esters include: methyl oxamate, ethyl oxamate, propyl oxamate, isopropyl oxamate, butyl oxamate and phenyl oxamate.

Preferably, the amine is 4-amino-2,2,6,6-tetramethylpiperidine, the oxamate ester is ethyl oxamate and the hydrazine is 85–100% hydrazine hydrate.

PREPARATION OF METHOD F

The compounds of Formula I where R^4 is a primary or secondary alkyl of 1 to 8 carbons, an aralkyl of 7 to 12 carbons or a cycloalkyl of 5 to carbons, designated generally by Formula XVIII, may be prepared by reacting ketone hydrazones of Formula XVI, such as acetone hydrazones of the corresponding hydrazines, with the half ester-half amides of Formulas IV to form the